Stability and behaviour of low level spiked inorganic mercury in natural water samples

Milena Horvat[1], Arne Bratkič[1], Janja Tratnik Snoj[1], Neža Koron[2], Sergio Ribeiro Guevara[3]

[1]Department of Environmental Sciences, "Jožef Stefan" Institute, Jamova 39, Ljubljana, Slovenia
[2]National institute of Biology, Piran, Slovenia
[3] Laboratorio de Análisis por Activación Neutrónica, Centro Atómico Bariloche, 8400 Bariloche, Argentina

In recent years tracer experiments using stable and radioactive mercury isotopes have been extensively used to understand Hg transformation processes in soils, sediments and water. Tracer experiments have also been used in method evaluations. Isotope dilution mass spectrometry (IDMS) is based on the use of enriched stable Hg isotopes, where a known mass of a spike of an enriched isotope is added to an aliquot of the sample prior to the pre-treatment procedures and the ratio of the added to the naturally occurring isotope is then measured. Although initially it was believed that this is the most powerful tool for the optimization and validation of analytical procedures, several reviews have outlined the advantages and limitations of IDMS approaches, among which contamination cannot fully be avoided, which is not the case with the use of radiolabelled Hg. An important obstacle in many of these experiments is that the quantity of labelled Hg used for spiking significantly exceeds the natural concentrations leading to significant perturbation of the system. The information obtained, therefore, may poorly represents the "natural" response.

The present study is focused on the use of $^{197}Hg^{2+}$ radiotracer (prepared from enriched ^{196}Hg) in natural water samples. Different samples were tested in the experiments including marine, lagoon, lake, river and rain waters. The purpose of these experiments was to test the stability and partitioning of labelled Hg^{2+} between dissolved and particulate-bound fractions under different storage conditions, namely temperature, preservation by acidification and container material (Teflon, borosilicate glass and polyethylene).

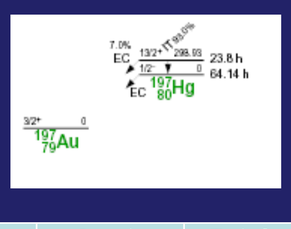
Experimental

STEP 1

Production of ^{197}Hg from enriched ^{196}Hg

Irradiation of Hg^{2+} in 2 % HNO_3 solution, in quartz ampoules

$^{196}Hg(n,\gamma)^{197}Hg$



	Probability of the (n.γ) reaction in thermal neutron flux (cross section)	Half life	Isotopic abundance	Typical specific activity (kBq μg^{-1})
^{197}Hg	3080 barns	64.14 h	natural, 0.15 %	22[a]
			enriched, 51 %	7700[a]
^{203}Hg	4.42 barns	46.595 d	natural, 6.87 %	15 to 60[b]

[a] Irradiation conditions: thermal neutron flux, $\phi_{th}=1\times10^{13}$ n cm^{-2} s^{-1}; irradiation time, 18 h; cooling time, 12 h.
[b] The irradiation of natural Hg produce about 50 times higher specific activity of ^{197}Hg than ^{203}Hg

STEP 2

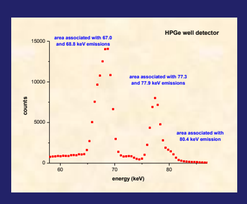
Spiking natural waters

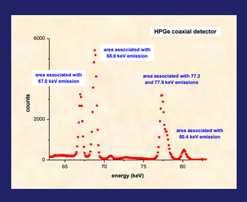
study case	labelled Hg concentration (ng L^{-1})			
	natural		acidified	
	refrigerator	room	refrigerator	room
coastal lagoon	5.0	5.0	3.8	3.5
marine	4.9	4.9	3.8	3.5
river	4.1	4.1	3.7	3.8
lake	4.4	4.4	3.0	2.9
rain	-	-	5.5	5.2
lake water in Teflon	12.6	12.6	12.5	12.3
lake water in glass	12.6	12.8	12.4	12.3
lake water in Polyethylene	12.7	12.1	11.9	11.6
marine water in Teflon	12.3	12.4	12.8	13.1
marine water in glass	12.1	12.2	12.3	12.4
marine water in Polyethylene	12.2	12.2	12.5	12.6
pH in lake water	-	8.5	-	-
pH in lake marine	-	8.4	-	-

STEP 3

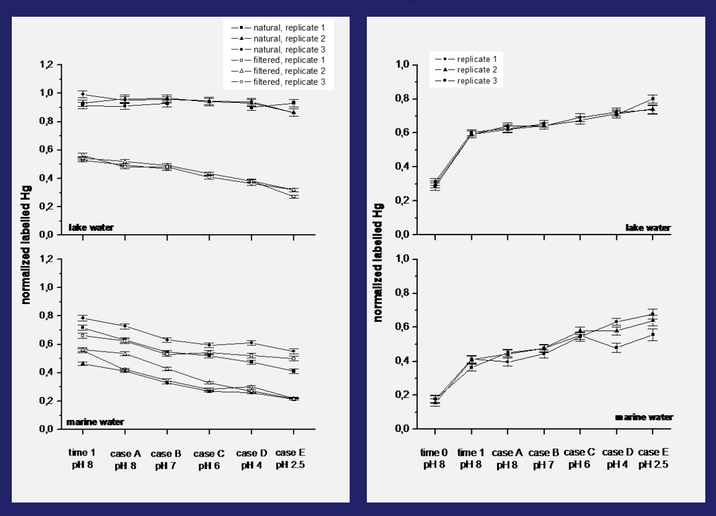
Detection:

High Purity Germanium Detector (Well type; Coaxial type)





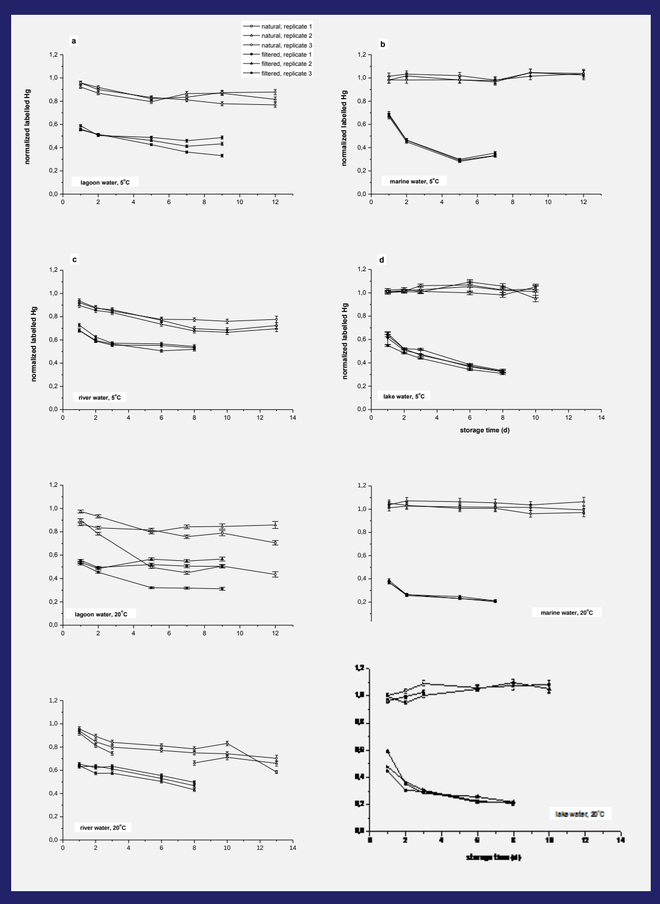
Fractionation of Hg in lake and marine waters as a function of pH



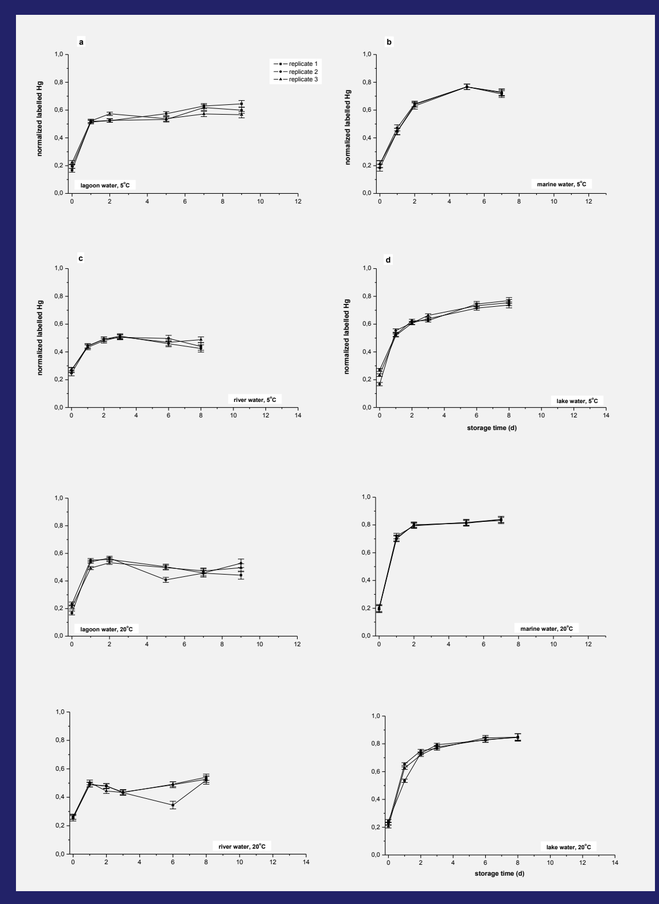
Results

The labelled Hg^{2+} concentrations are normalized to the initial concentration

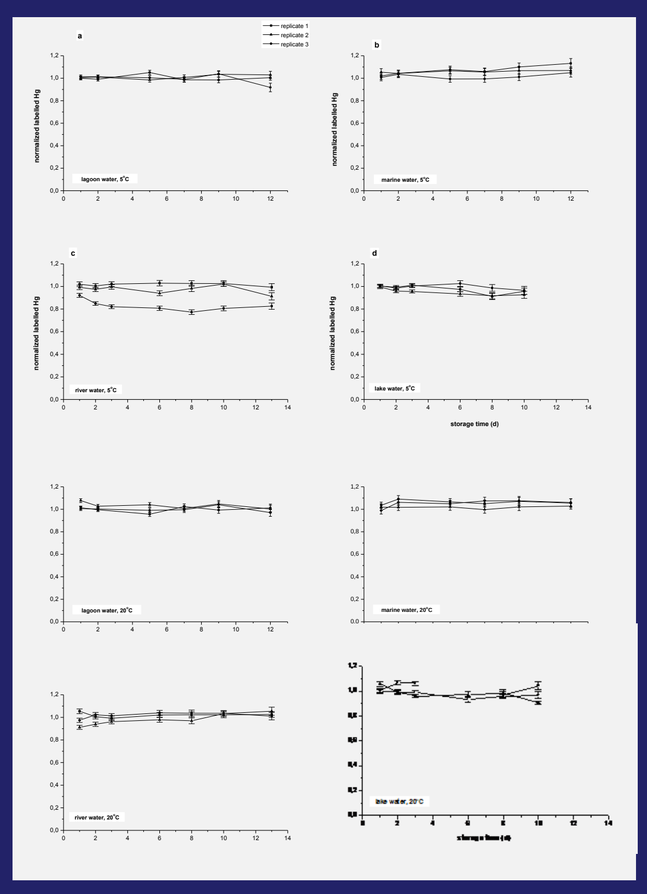
Stability and partitioning of labelled Hg^{2+} in water samples as a function of time and storage temperature



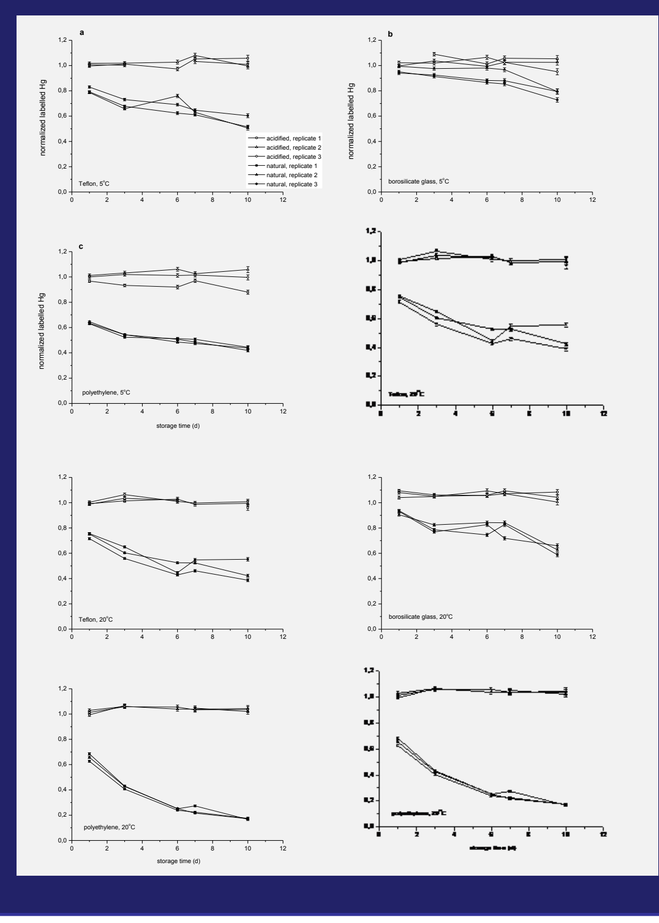
Transfer of labelled Hg^{2+} on suspended solids as a function of time and storage



Stability of labelled Hg^{2+} in waters preserved by acidification



Stability of labelled Hg^{2+} in natural and acidified marine waters stored in different containers



Conclusions

The practical implications of these experiments is that studies using tracer experiments in natural water need to be done with great care, taking into account the particular characteristics of the water under study. The use of $^{197}Hg^{2+}$ provides accurate results, enabling fast testing of different parameters and conditions.

References

Ribeiro Guevara S, Žižek S, Repinc U, Pérez Catán S, Jaćimović R, Horvat M. Novel methodology for the study of mercury methylation and reduction in sediments and water using ^{197}Hg radiotracer. Analytical and Bioanalytical Chemistry 387 No.6 (2007) 2185-2197.

Žižek S, Ribeiro Guevara S, Horvat M. Validation of methodology for determination of the mercury methylation potential in sediments using radiotracers. Analytical and Bioanalytical Chemistry 390 (2008) 2115–2122